

ARSENIC IS UBIQUITOUS BUT NOT ELEVATED IN ABANDONED COAL-MINE DISCHARGES IN PENNSYLVANIA

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ABSTRACT

Despite elevated concentrations in coal beds, dissolved As rarely is elevated in abandoned coal-mine discharges in Pennsylvania. For 140 samples collected in 1999, concentrations of As ranged from <0.03 to 15 µg/L in 41 anthracite mine discharges and from 0.10 to 64 µg/L in 99 bituminous coal-mine discharges. The pH of these discharges ranged from 2.7 to 7.3, with dominant modes at pH 3-4 and 6-7; concentrations of Fe ranged from 46 to 512,000 mg/L. The As was positively correlated with pH, alkalinity, Fe, SO₄, Cl, Br, and I and was inversely correlated with redox potential. Aqueous speciation computations indicated arsenate species (H₂AsO₄⁻ and HAsO₄²⁻) predominated.

Concentrations of As in Fe-rich precipitate (ochre) samples from 20 of the anthracite discharge sites ranged from <0.07 to 270 mg/kg. Generally, the concentration of As in the solids was positively correlated with the concentration of As and pH of the source water; the ratio of As concentrations in solution to As in solids (K_d) did not vary with pH. This trend could indicate increased capacity for attenuation of As by Fe compounds at higher pH. Poorly crystalline Fe(III) oxyhydroxides, such as ferrihydrite, tend to form under near-neutral conditions whereas Fe(III) oxyhydroxysulfates, such as schwertmannite, and crystalline Fe(III) oxyhydroxides, such as goethite, are predominant Fe(III) phases formed at low pH. Ferrihydrite could have greater sorption capacity for arsenate than goethite or schwertmannite. Nevertheless, the As that is associated with metastable Fe(III) compounds, such as ferrihydrite and schwertmannite, can be remobilized (1) upon conversion of metastable compounds to more stable phases such as goethite or (2) from reductive dissolution or acidic digestion.

ARSENIC IN ABANDONED MINE DISCHARGES, ANTHRACITE AND BITUMINOUS COALFIELDS

PHYSIOGRAPHIC SETTING

Bituminous coal deposits underlie western and north-central Pennsylvania, and anthracite deposits underlie east-central and northeastern Pennsylvania (see map). The mineable coals, mostly of Pennsylvanian Age, are interbedded with shale, siltstone, sandstone, and occasional limestone (Brady and others, 1998). The bituminous coalfield lies within the Appalachian Plateaus Physiographic Province and is characterized by gently dipping strata (Berg and others, 1989); nearly horizontal coalbeds commonly crop out in the incised stream valleys. The anthracite coalfield lies within the adjacent Ridge and Valley Physiographic Province, which is characterized by complexly deformed strata (Wood and others, 1986). Mineable anthracite beds are present primarily in steeply folded and fractured synclinal troughs.

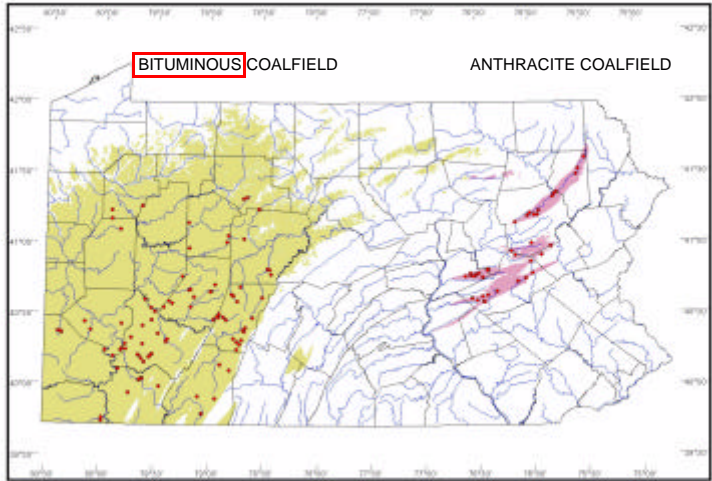
CLEAN METHODS FOR WATER SAMPLING & ANALYSIS

A two-person USGS team collected global positioning system (GPS) coordinates, hydrological, and chemical data for each sampling station. Field data for flow rate, pH, redox potential (Eh), specific conductance, dissolved oxygen, and temperature were measured when samples were collected using field-calibrated instruments (Wilde and others, 1998). The team used low-level (part per billion, part per trillion) techniques for sampling and analysis (Horowitz and others, 1994; Wilde and others, 1998). Samples for analysis of dissolved inorganic constituents were filtered using 0.45-µm capsule filters.

Alkalinity and acidity on unfiltered samples were determined in the laboratory within 48 hours of sampling. Concentrations of major anions, major cations, and trace elements were determined using inductively coupled plasma emission mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and ion chromatography (IC) (Fishman and Friedman, 1989; Faires, 1993). All samples were analyzed in replicate. Split samples were analyzed at the USGS Mineral Resources Laboratory in Denver and Activation Laboratories in Canada, and a subset was analyzed by the USGS National Water Quality Laboratory.

SITES SELECTED ON BASIS OF FLOW & CHEMISTRY

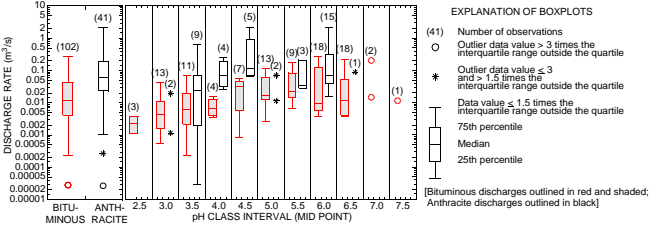
Selected large discharges from abandoned underground mines were sampled by the U.S. Geological Survey (USGS) during low-flow conditions in 1999. The 101 bituminous discharges had previously been studied by the Southern Alleghenies Conservancy (1998). The 41 anthracite discharges had previously been studied by the USGS (Growitz and others, 1985; Wood, 1996).



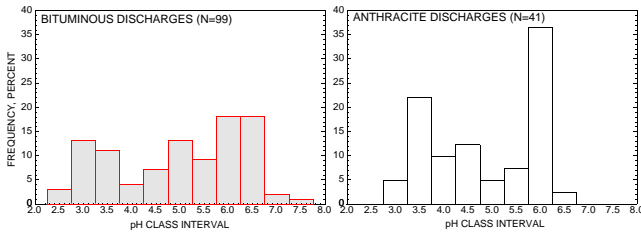
Geology from Berg and others (1990)

FLOW AND HYDROCHEMICAL CHARACTERISTICS

Flow from anthracite mines generally exceeds that from the bituminous mines sampled



All mine discharges are not acidic; dominant field pH classes are near neutral



Sulfate is the predominant solute

Chloride, bicarbonate, calcium, magnesium, and iron generally are elevated. Arsenic is ubiquitous, but present in relatively low concentrations; 85 percent of samples have As < 10 µg/L.

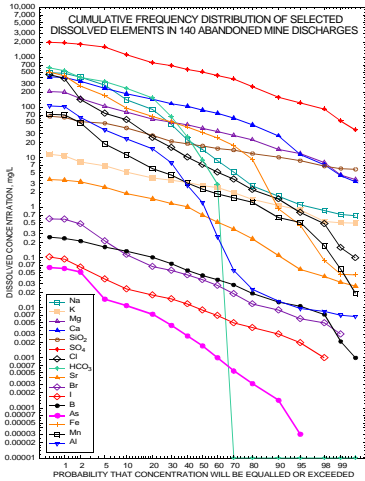


Table 2. Composition of discharges from abandoned coal mines in Pa., 1999 [median (minimum-maximum)]

Coalfield & number of samples	Arsenic (mg/L)	pH	Eh (mV)	Oxygen	Sulfate	Iron	Manganese
				(mg/L)	(mg/L)	(mg/L)	(mg/L)
Anthracite N=41	0.62 (<0.03-15)	5.1 (3.0-6.3)	390 (170-770)	1.9 (0.3-11.1)	260 (36-1,300)	15 (0.046-312)	2.9 (0.019-19)
Bituminous N=99	2.0 (0.1-64)	5.2 (2.7-7.3)	340 (140-800)	0.6 (0.2-11.5)	580 (120-2,000)	43 (0.16-512)	2.3 (0.12-74)

Bituminous discharges generally have higher arsenic concentrations than anthracite discharges. This suggests a link to the high concentrations of arsenic in bituminous coal.

ARSENIC IN PENNSYLVANIA COALS

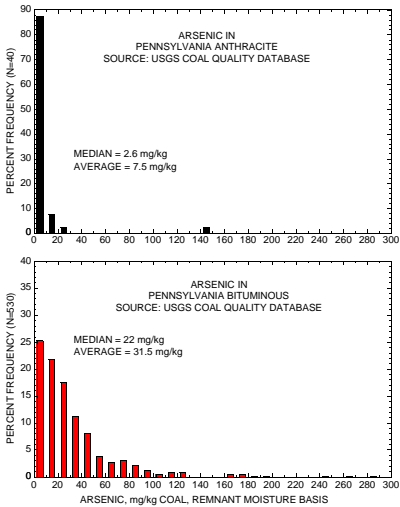
Shales contain the highest concentration of arsenic in the principal types sedimentary rocks (see table). Anthracite coals in Pennsylvania contain less arsenic than an average shale. Bituminous coals in Pennsylvania are enriched in arsenic relative to anthracite coal and shale. Histograms of arsenic data for 530 channel samples of Pennsylvania bituminous and 40 samples of Pennsylvania anthracite (from USGS Coal Quality database) show the arsenic concentration distributions in the two coal types.

Arsenic is present in sulfide minerals in the coal beds. When the beds are disturbed by mining, the arsenic may be leached or solubilized by waters that flood the abandoned mines.

Table 1. Arsenic Abundance In Principal Sedimentary Rocks (ppm)

Crustal Average	Shales	Sandstones	Carbonates	Igneous Rocks
5	13	1	1	1.8

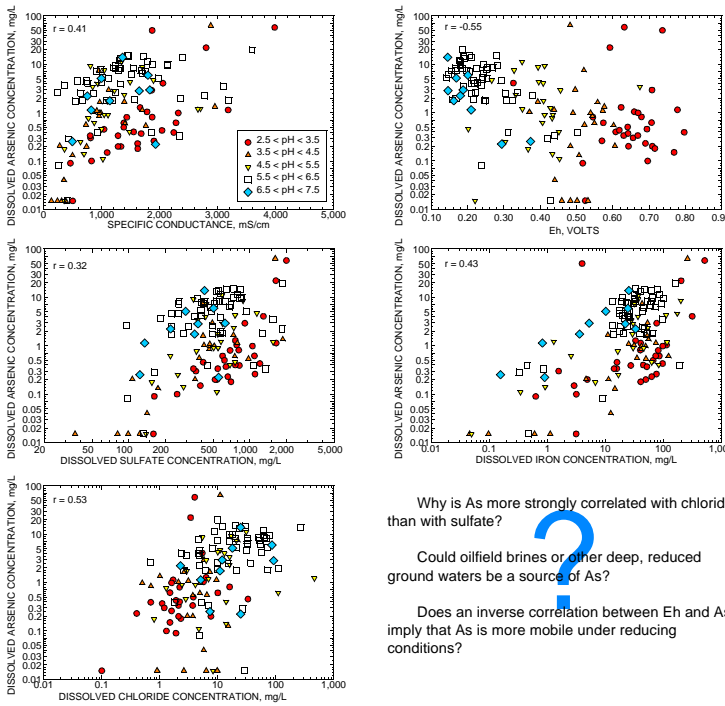
Data Source: Mason (1966)



Conclusion: The coals and associated shales in the coal-bearing strata in Pennsylvania are a source of arsenic when the strata are disturbed in the mining process.

Hypothesis: Given the high amount of arsenic in bituminous coal relative to anthracite, the waters that discharge from abandoned bituminous coal mines will have more arsenic than waters that discharge from abandoned anthracite mines.

Arsenic concentration increases with increases in dissolved constituents; questions about arsenic mobility and its source remain to be answered



Why is As more strongly correlated with chloride than with sulfate?

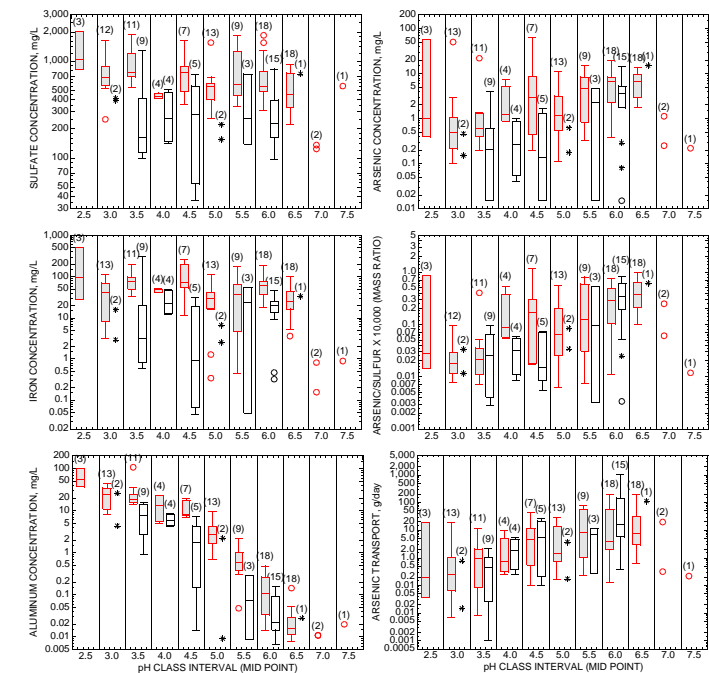
Could oilfield brines or other deep, reduced ground waters be a source of As?

Does an inverse correlation between Eh and As imply that As is more mobile under reducing conditions?

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ARSENIC ATTENUATION AND CHARACTERISTICS OF THE SOLID PHASES

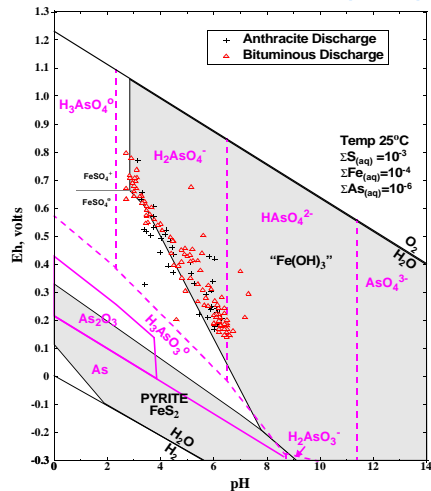
pH and other chemical characteristics vary due to
pyrite oxidation and neutralization processes



Why is the concentration of As for bituminous discharges elevated compared to anthracite discharges?

Does dilution or neutralization attenuate arsenic concentration and loading?

Arsenate and ferrous species predominate



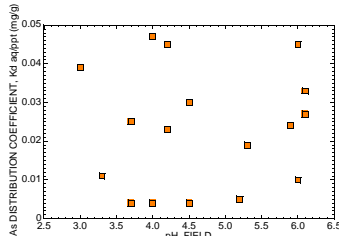
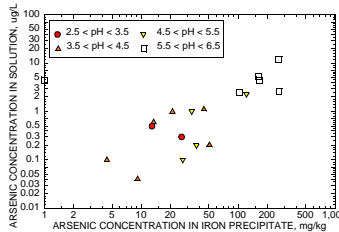
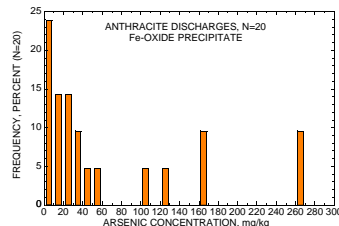
Bowell (1994) reported mineralogy and As speciation affect attenuation.

Hereafter, "Fe(OH)₃" indicates the hydrous Fe-oxide and -sulfate compounds that together form ochres in mine drainage environments, including Fe(OH)₃ or ferrihydrite (nominally Fe₅HO₈·4H₂O), goethite (α-FeOOH), and schwertmannite (Fe₈O₈(OH)₆SO₄) (Bigham and others, 1996; Yu and others, 1999).

PRECIPITATE MINERALOGY & CHEMISTRY FOR SOME SITES

Samples of accumulated ochre (iron-oxide precipitate) that was in contact with the mine water were collected in October 1997 at a few of the Anthracite discharge sites by J. Bigham and D.J. Williams (Ohio State University). The mineralogy of these samples was determined by X-ray diffraction. Twenty samples of precipitate were collected in 1999 at the time of the discharge water sampling and analyzed for arsenic by Jim Budahn (USGS-Denver).

Concentration of As in ochre samples increases with increasing concentration of As in solution.

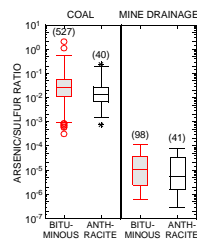


Why are highest concentrations of As in ochre samples associated with near-neutral pH discharges?

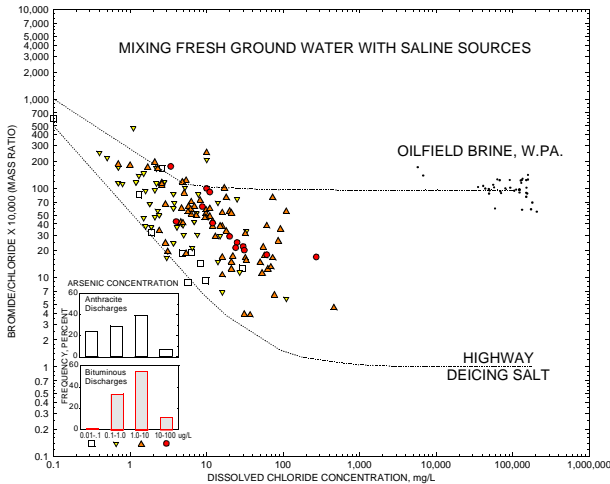
Would concentrations of As in bituminous ochres be elevated compared to anthracite ochres?

The As/S ratio in coal is 1,000 times that of mine drainage.

This indicates that As attenuation results mainly from adsorption and not from dilution. (Congruent dissolution and dilution with pure water would not affect ratio.)

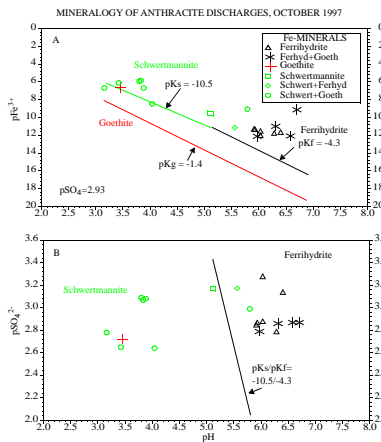


Bromide/chloride relations indicate possible arsenic contributions from interaction with saline sources



Sources of information: Whittemore (1988) and Dresel (1985)

Ochre mineralogy varies as function of pH and activities of Fe³⁺ and SO₄²⁻



Observed ochre mineralogy is consistent with aqueous activities and mineral solubilities as reported by Bigham and others (1996), Yu and others (1999), and Williams and others (in review).

Ferrihydrite predominates at near-neutral pH; schwertmannite and goethite dominate at acidic pH.

SUMMARY

Coal and discharges from bituminous mines generally have greater concentrations of As and S than those from anthracite mines.

The majority of bituminous and anthracite discharges has near-neutral pH. Near-neutral and acidic discharges have elevated concentrations of SO₄, Fe, and other solutes.

Compared to other solutes in mine discharges, concentration of As is low, with a reported maximum of 65 μg/L for 140 discharges sampled for this study.

Although the two highest concentrations of As were in low-pH and high-Eh discharges, generally concentration of As increased with increased pH (and decreased Eh).

An inverse correlation exists for As with Eh; there is a positive correlation for As with Cl and other halides, pH, Fe, and SO₄ (in order of decreased significance).

IMPLICATIONS

Dissolved As in mine discharges results from:

(1) weathering of pyrite and other minerals associated with coal deposits under oxidizing conditions and

(2) reductive dissolution of oxides along flow paths of deep, reducing ground waters.

Attenuation of As in mine discharges results from:

(1) adsorption to ochre-forming "Fe(OH)₃" that precipitates under oxidizing conditions,

(2) and, to a lesser degree, dilution.

Although the As content of bituminous ochres is unknown, higher As concentrations in bituminous coal and discharges compared to anthracite could result in ochres that contain greater As concentrations than anthracite ochres.

As-rich ochres precipitated by mine discharges can (1) accumulate in wetlands and other accessible water bodies and (2) can be scoured and transported to downstream waters where they are subject to ingestion by aquatic organisms and reductive dissolution.

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